

PATENT ABSTRACTS OF JAPAN

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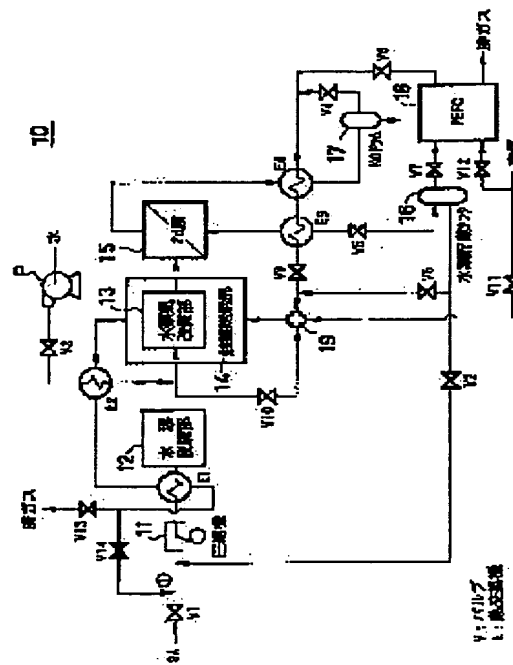
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(54) HYDROGEN MANUFACTURING EQUIPMENT STARTUP METHOD AND ITS SHUTDOWN METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a startup method and a shutdown method of hydrogen manufacturing equipment, which enables to reduce running cost and installing area and to eliminate such dangerous work as exchange of nitrogen and hydrogen bombs.

SOLUTION: At startup, a steam reforming part 13 is elevated in temperature through a catalyst combustion reaction by supplying highly pure hydrogen in a hydrogen storage tank 16 and air to a catalyst combustion chamber 14. When the temperature is elevated to the level of starting steam reforming, supply of steam, hydro-desulfurization and law material of hydrocarbon is begun. At shutdown, density of oxygen in the catalyst chamber 14 is reduced, and combustion gas is recycled to reaction system to gradually reduce density of combustible gas. Replacing with nitrogen, carbon dioxide and steam finally, the operation is shutdown. As a result, operation cost and installing area can be reduced, and such dangerous work as exchanging nitrogen and hydrogen bombs can be eliminated.



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CLAIMS

[Claim(s)]

[Claim 1] The desulfurization section which removes the sulfur content of coal-for-coke-making-ized hydrogen, and the steam-reforming section which generates hydrogen content gas by adding and carrying out steam reforming of the steam to the coal-for-coke-making-ized hydrogen desulfurized in the above-mentioned desulfurization section, The hydrogen purification section which penetrates the hydrogen in the above-mentioned hydrogen content gas by the inorganic hydrogen demarcation membrane, and manufactures purification hydrogen, In the starting approach of the hydrogen manufacturing installation equipped with the catalyzed combustion section which is made to carry out the combustion reaction of the inflammable gas of hydrogen content, and the oxygen in air, and heats the above-mentioned steam-reforming section When the temperature up of the above-mentioned steam-reforming section is carried out by supplying the purification hydrogen and air which were refined in the above-mentioned hydrogen purification section to the above-mentioned catalyzed combustion section, and making it cause a catalyzed combustion reaction and the temperature of the above-mentioned steam-reforming section reaches the initiation temperature of steam reforming, The starting approach of the hydrogen manufacturing installation which starts supply of the above-mentioned steam and the above-mentioned coal-for-coke-making-ized hydrogen.

[Claim 2] The above-mentioned purification hydrogen is the starting approach of the hydrogen manufacturing installation according to claim 1 supplied to a fuel cell.

[Claim 3] The starting approach of the hydrogen manufacturing installation according to claim 1 or 2 which is the hydrogenation-desulfurization section from which the above-mentioned desulfurization section desulfurizes and removes the sulfur content in the above-mentioned coal-for-coke-making-ized hydrogen after adding the hydrogen for hydrogenation desulfurization in coal-for-coke-making-ized hydrogen.

[Claim 4] The starting approach of a hydrogen manufacturing installation given in any 1 term among claims 1 - claims 3 which have the hydrogen stores dept. which stores the purification hydrogen obtained from the above-mentioned hydrogen purification section.

[Claim 5] The desulfurization section which removes the sulfur content of coal-for-coke-making-ized hydrogen, and the steam-reforming section which generates hydrogen content gas by adding and carrying out steam reforming of the steam to the coal-for-coke-making-ized hydrogen desulfurized in the above-mentioned desulfurization section, The hydrogen purification section which penetrates the hydrogen in the above-mentioned hydrogen content gas by the inorganic hydrogen demarcation membrane, and refines purification hydrogen, In the halt approach of the hydrogen manufacturing installation equipped with the catalyzed combustion section which is made to carry out the combustion reaction of the inflammable gas of hydrogen content, and the oxygen in air, and heats the above-mentioned steam-reforming section Lower gradually the amount of supply of the air to the above-mentioned catalyzed combustion section, and the oxygen density in the combustion gas discharged from this catalyzed combustion section is reduced. Supplying the combustion gas from this catalyzed combustion section in the system of reaction of a hydrogen manufacturing installation, and reducing gradually the amount of supply of the above-mentioned coal-for-coke-making-ized hydrogen and a steam The halt approach of a hydrogen manufacturing installation which the concentration of the inflammable gas in this system of reaction is reduced, and suspends supply of the air to the above-mentioned catalyzed combustion section after that, and stops the above-mentioned hydrogen manufacturing installation after the temperature in the above-mentioned system of reaction falls.

[Claim 6] The above-mentioned purification hydrogen is the halt approach of the hydrogen manufacturing installation according to claim 5 supplied to a fuel cell.

[Claim 7] The halt approach of the hydrogen manufacturing installation according to claim 5 or 6 which is the hydrogenation-desulfurization section from which the above-mentioned desulfurization section desulfurizes and removes the sulfur content in the above-mentioned coal-for-coke-making-ized hydrogen after adding the hydrogen for hydrogenation desulfurization in coal-for-coke-making-ized hydrogen.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to starting and the halt approach of the hydrogen manufacturing installation containing the steam-reforming section, or the hydrogen manufacturing installation used for a fuel cell system or the other application.

[0002]

[Description of the Prior Art] General starting and halt of a hydrogen manufacturing installation use inert gas, such as nitrogen with which the bomb was filled up. the time of starting -- a bomb -- hydrogen is supplied for nitrogen from a hydrogen bomb as a temperature up and hydrogenation gas for desulfurization by a burner etc. with a sink in a system. At the time of a halt, after nitrogen permutes inflammable gas, temperature fall actuation is performed. With this method, while being able to prevent oxidization of a catalyst, and the hydrogen embrittlement of metal membranes, such as palladium film, it can be operated safely. However, there is a trouble that a nitrogen gas cylinder, a hydrogen bomb, etc. are required, and cost quantity and an installation tooth space become large as a fault of this method. Moreover, when short of inert gas, starting / halt actuation cannot be performed, but exchange of a bomb is troublesome, and since it is high pressure, it is dangerous. In addition, under small equipment (for example, home use and the hydrogen manufacturing installation for fuel cells for mount), many situations, etc., also when neither a nitrogen gas cylinder nor a hydrogen bomb can be installed, it thinks, and there is also a trouble of the infrastructure of hydrogen and nitrogen not being fixed further.

[0003] In addition, after suspending supply of coal-for-coke-making-ized hydrogen and lowering the temperature gradually to extent to which a catalyst does not oxidize, how to permute with air is also considered. However, according to this approach, in order to supply air into inflammable gas, we are anxious about the problem that it is accompanied by risk. In addition, since the gas containing hydrogen is supplied to inorganic hydrogen demarcation membranes, such as palladium film, at low temperature, hydrogen embrittlement tends to happen. Consequently, we are anxious also about the problem of becoming lacking in the endurance of an inorganic hydrogen demarcation membrane. Furthermore, although heating of the steam-reforming section has common use of a burner, when inflammable-gas concentration falls, there is a trouble that combustion will stop.

[0004]

[Problem(s) to be Solved by the Invention] It is troublesome and offers the starting approach of the hydrogen manufacturing installation which can also reduce the time amount which exchange of the bomb accompanied by risk takes, and its halt approach while it can attain miniaturization of equipment since this invention was made against the background of such a conventional technique, and does not need bombs, such as a nitrogen gas cylinder and a hydrogen bomb, in a hydrogen manufacturing installation, reduction of cost can be aimed at and the installation tooth space of a bomb becomes unnecessary. Moreover, this inventions are the domestic-fuel cell which cannot install a bomb, the fuel cell for mount and other fuel cells, an on-site hydrogen manufacturing installation, etc., and neither a hydrogen bomb, a nitrogen gas cylinder and a burner nor special power is used for them, but they set it as the purpose to offer the starting approach of a safe hydrogen manufacturing installation, and its halt approach.

[0005]

[Means for Solving the Problem] The desulfurization section from which invention according to claim 1 removes the sulfur content of coal-for-coke-making-ized hydrogen, The steam-reforming section which generates hydrogen content gas by adding and carrying out steam reforming of the steam to the coal-for-coke-making-ized hydrogen desulfurized in the above-mentioned desulfurization section, The hydrogen

purification section which penetrates the above-mentioned hydrogen in hydrogen content gas by the inorganic hydrogen demarcation membrane, and manufactures purification hydrogen. In the starting approach of the hydrogen manufacturing installation equipped with the catalyzed combustion section which is made to carry out the combustion reaction of the inflammable gas of hydrogen content, and the oxygen in air, and heats the above-mentioned steam-reforming section. When the temperature up of the above-mentioned steam-reforming section is carried out by supplying the purification hydrogen and air which were refined in the above-mentioned hydrogen purification section to the above-mentioned catalyzed combustion section, and making it cause a catalyzed combustion reaction and the temperature of the above-mentioned steam-reforming section reaches the initiation temperature of steam reforming, It is the starting approach of the hydrogen manufacturing installation which starts supply of the above-mentioned steam and the above-mentioned coal-for-coke-making-ized hydrogen.

[0006] Invention according to claim 2 is the starting approach of a hydrogen manufacturing installation according to claim 1 that the above-mentioned purification hydrogen is supplied to a fuel cell.

[0007] Invention of claim 3 is the starting approach of a hydrogen manufacturing installation according to claim 1 or 2 that the above-mentioned desulfurization section is the hydrogenation-desulfurization section which desulfurizes and removes the sulfur content in the above-mentioned coal-for-coke-making-ized hydrogen after adding the hydrogen for hydrogenation desulfurization in coal-for-coke-making-ized hydrogen.

[0008] Invention of claim 4 is the starting approach of a hydrogen manufacturing installation given in any 1 term among claims 1 - claims 3 which have the hydrogen stores dept. which stores the purification hydrogen obtained from the above-mentioned hydrogen purification section.

[0009] The desulfurization section from which invention according to claim 5 removes the sulfur content of coal-for-coke-making-ized hydrogen, The steam-reforming section which generates hydrogen content gas by adding and carrying out steam reforming of the steam to the coal-for-coke-making-ized hydrogen desulfurized in the above-mentioned desulfurization section, The hydrogen purification section which penetrates the hydrogen in the above-mentioned hydrogen content gas by the inorganic hydrogen demarcation membrane, and refines purification hydrogen, In the halt approach of the hydrogen manufacturing installation equipped with the catalyzed combustion section which is made to carry out the combustion reaction of the inflammable gas of hydrogen content, and the oxygen in air, and heats the above-mentioned steam-reforming section. Lower gradually the amount of supply of the air to the above-mentioned catalyzed combustion section, and the oxygen density in the combustion gas discharged from this catalyzed combustion section is reduced. Supplying the combustion gas from this catalyzed combustion section in the system of reaction of a hydrogen manufacturing installation, and reducing gradually the amount of supply of the above-mentioned coal-for-coke-making-ized hydrogen and a steam. After reducing the concentration of the inflammable gas in this system of reaction, suspending supply of the air to the above-mentioned catalyzed combustion section after that and the temperature in the above-mentioned system of reaction falling, it is the halt approach of a hydrogen manufacturing installation which stops the above-mentioned hydrogen manufacturing installation.

[0010] Invention according to claim 6 is the halt approach of a hydrogen manufacturing installation according to claim 5 that the above-mentioned purification hydrogen is supplied to a fuel cell.

[0011] Invention of claim 7 is the halt approach of a hydrogen manufacturing installation according to claim 5 or 6 that the above-mentioned desulfurization section is the hydrogenation-desulfurization section which desulfurizes and removes the sulfur content in the above-mentioned coal-for-coke-making-ized hydrogen after adding the hydrogen for hydrogenation desulfurization in coal-for-coke-making-ized hydrogen.

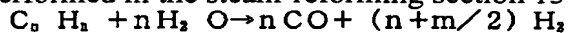
[0012]

[Embodiment of the Invention] The gestalt of implementation of invention is explained based on a drawing. Drawing 1 is the schematic diagram showing the starting approach of the hydrogen manufacturing installation concerning the gestalt of 1 operation of this invention. Drawing 2 is the schematic diagram showing the halt approach of the hydrogen manufacturing installation concerning the gestalt of 1 operation of this invention. In drawing 1, a sign 10 is a hydrogen manufacturing installation which uses town gas, LPG, kerosene, a methanol, etc. as a raw material. In addition, town gas is adopted here. Hereafter, each configuration section of this hydrogen manufacturing installation 10 is explained. A sign 11 is a compressor which supplies town gas to the hydrogenation-desulfurization section (desulfurization section) 12. This hydrogenation-desulfurization section 12 is divided into the hydrogenation catalyst layer of the upstream, and the purifier grids of the downstream. In the hydrogenation-desulfurization section 12, the sulfur content in town gas is desulfurized by adding a part of high grade hydrogen (purification hydrogen) obtained by

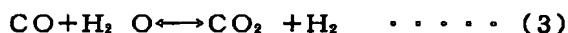
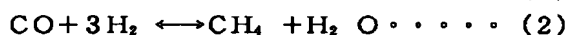
penetrating the palladium film (inorganic hydrogen demarcation membrane) of the high grade hydrogen purification section (hydrogen purification section) 15 later mentioned to the town gas supplied by the compressor 11 as hydrogen for hydrogenation desulfurization.

[0013] As a hydrogenation catalyst, a NiMox catalyst or a CoMox catalyst etc. which made support, such as a silica and an alumina, support oxides, such as nickel-molybdenum or cobalt-molybdenum, or a sulfide is mentioned. Under low voltage, a nickel-molybdenum catalyst is desirable. Moreover, as a devulcanizing agent, a zinc oxide, a nickel system sorbing agent, etc. are supported and used for independent or proper support. In a hydrogenation catalyst layer, the sulfur content in coal-for-coke-making-ized hydrogen is hydrogenated and a hydrogen sulfide generates. The reaction temperature is 300-400 degrees C, is desulfurizing using high grade hydrogen, and will also go up the desulfurization effectiveness, and the life of a reforming catalyst will also be prolonged. In purifier grids, the reaction of $\text{H}_2\text{S} + \text{ZnO} = \text{ZnS} + \text{H}_2\text{O}$ occurs, for example. In addition, the coal-for-coke-making-ized hydrogen after desulfurization is supplied to the steam-reforming section 13. Here, although the hydrogenation-desulfurization approach was adopted for the sulfur compound in coal-for-coke-making-ized hydrogen, the approach of making a sulfur compound sticking to a catalyst directly may be used. As a catalyst in this case, a zeolite, activated carbon, etc. are mentioned, for example to metals and the oxides of those, such as nickel, zinc, and copper, or a sulfide, and a pan. As activated carbon, what installed alkali metal, such as sodium, the activated carbon which adsorbed the bromine can be used.

[0014] This steam-reforming section 13 adds water or a steam to the desulfurized town gas, is that contact a reforming catalyst and it carries out steam reforming further, and manufactures high concentration hydrogen content gas. This steam-reforming section 13 is filled up with the reforming catalyst which supported elements, such as a ruthenium or nickel, to support, such as an alumina and a silica. Among these, when the direction of a ruthenium system catalyst uses raw materials, such as kerosene with many carbon numbers, since a carbon deposit can be controlled, it is desirable. Steam reforming of the desulfurized hydrocarbon is performed in the steam-reforming section 13. A reaction here is shown below.



..... (1)



[0015] A sign 14 is the catalyzed combustion section to which sheathing is carried out to the perimeter of the steam-reforming section 13, and catalyzed combustion of hydrogen and the oxygen in air is carried out. In addition, the interior of the catalyzed combustion section 14 may be carried out to the steam-reforming section 13, and the reactor of a heat exchange mold with still higher heat-conducting characteristic etc. is sufficient as it. The catalyst which supported platinum, palladium, etc. is used for an alumina etc. as a catalyst of the catalyzed combustion section 14. The temperature of the steam-reforming section 13 at the time of starting of the hydrogen manufacturing installation 10 is 380 degrees C or more, for example, 380-500 degrees C. At less than 380 degrees C, a reaction invert ratio is low, and in case the inflammable gas containing hydrogen, methane, a carbon monoxide, etc. is reused in the catalyzed combustion section, unarranging [that oxidation reaction of these inflammable gas does not progress] arises. And finally about 800 degrees C is desirable.

[0016] The desirable addition rates of a steam are a steam / raw material (S/C) 2.4 - 3.0 kg-mol-H₂O/kg-mol-C. It is 2.5 - 2.8 kg-mol-H₂O/kg-mol-C still more preferably. Under by 2.4 kg-mol-H₂O/kg-mol-C, the reaction invert ratio of town gas becomes low, and while the amount of hydrogen purification falls, carbon also becomes easy to deposit. On the other hand, if 3.0 kg-mol-H₂O/kg-mol-C is exceeded, although the reaction invert ratio of town gas increases, since there are many amounts of steam and a hydrogen partial pressure falls, it is disadvantageous for hydrogen membrane separation by the palladium film.

[0017] A sign 15 is the high grade hydrogen purification section which penetrates the hydrogen in high concentration hydrogen content gas by the palladium film, and refines high grade hydrogen. What covered the palladium alloy film which consists of an alloy with palladium, silver and copper, nickel, an yttrium, etc. besides this palladium film as an inorganic hydrogen demarcation membrane to various kinds of independent or porosity support, such as a product made from the ceramics, glass, and stainless steel, the zeolite film, etc. are employable.

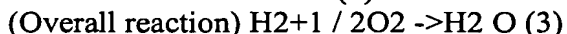
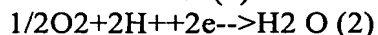
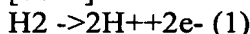
[0018] A sign 16 is a hydrogen storage tank (hydrogen stores dept.) which stores the high grade hydrogen obtained from the high grade hydrogen purification section 15. In order that the hydrogen storage tank 16

shall store the hydrogen of a complement in the object for catalyzed combustion, and hydrogenation gas at the time of starting and may attain miniaturization, its tank by which it filled up with the hydrogen storing metal alloy is desirable.

[0019] A sign 17 is a KO (knock out) drum from which the moisture which cools the nontransparent gas of the above-mentioned palladium film, and is contained in this gas is removed.

[0020] A sign 18 is a polymer electrolyte fuel cell (henceforth a fuel cell 18) with which the high grade hydrogen by which temporary storage was carried out to the hydrogen storage tank 16 is supplied. As the application, a domestic-fuel cell, the fuel cell for mount, etc. are mentioned, for example. This fuel cell 18 has the electrolyte ingredient. This electrolyte ingredient has the macromolecule ion exchange membrane which generally has a sulfonic acid group as an ion exchange group. If hydrogen (fuel) and oxygen (oxidizer) are supplied to a cel, electrical energy can be taken out to the exterior by the reaction of a degree type.

[0021]



The hydrogen ion generated by the formula (1) moves with water ($x\text{H}_2\text{O}$) through the ion exchange group in macromolecule ion exchange membrane, reacts with oxygen like a formula (2), and generates water (H_2O). The high grade hydrogen from which the impurity was removed is supplied to a fuel cell 18, after moisture adjustment is carried out, and electrical energy is obtained, generating water here. Since high grade hydrogen is supplied to the cel of a fuel cell 18, there is no electrode poisoning by the carbon monoxide, and degradation can be prevented. Moreover, the exhaust gas of a cel is made to supply to the catalyzed combustion section 14, and is used as a heat source in the system of reaction. In addition, it is reusable also as hydrogen for hydrogenation desulfurization. In addition, the air (oxygen) discharged from this fuel cell 18 may be supplied to the catalyzed combustion section 14.

[0022] A notation E1 is a heat exchanger which carries out heat exchange of the town gas supplied to the hydrogenation-desulfurization section 12 from a compressor 11, and the combustion gas from the catalyzed combustion section 14, and raises town gas to the hydrogenation-desulfurization temperature of 300-400 degrees C. A notation E2 is a heat exchanger which heat exchange of the water supplied to the steam-reforming section 13 by feed-pump P and the combustion gas from the catalyzed combustion section 14 is carried out [heat exchanger], and generates the steam for steam reforming. A notation E3 is a heat exchanger which carries out heat exchange of the nontransparent gas of the part for a surplus and the palladium film of the high grade hydrogen supplied to the catalyzed combustion section 14 from a fuel cell 18, and the hot high grade hydrogen which penetrated the palladium film. A notation E4 is a heat exchanger which carries out heat exchange of the nontransparent gas of the part for a surplus and the palladium film of the high grade hydrogen supplied to the catalyzed combustion section 14 from a fuel cell 18, and the hot nontransparent gas of the palladium film. The inflammable gas containing the hydrogen reused by the catalyzed combustion section 14 by heat exchangers E3 and E4, methane, and a carbon monoxide is made into 380 degrees C or more heating and a temperature up. At less than 380 degrees C, it is because oxidation reaction of inflammable gas, such as methane, is not performed smoothly.

[0023] In addition, the hydrogen manufacturing installation 10 here consists of a compressor 11, the hydrogenation-desulfurization section 12, the steam-reforming section 13, the catalyzed combustion section 14, the high grade hydrogen purification section 15, and a hydrogen storage tank 16. However, the gas conversion section which is not illustrated in the latter part of the steam-reforming section 13 may be prepared. Moreover, you may make it the membrane reactor which unified the steam-reforming section 13 and the high grade hydrogen purification section 15, and the membrane reactor which united CO conversion section and the high grade hydrogen purification section 15 with the latter part of the steam-reforming section 13 may be prepared further. A sign 19 is passage switch equipment (henceforth the method valve of four) of the method valve format of four among drawing.

[0024] The starting approach of the hydrogen manufacturing installation 10 of the above-mentioned configuration and its halt approach are explained in full detail below. First, the actuation at the time of starting is explained based on drawing 1. As shown in drawing 1, a bulb V11 is opened and the catalyzed combustion section 14 is supplied through [method valve of four 19] the air besides a system. Subsequently, a bulb V6 is opened and high grade hydrogen is supplied to the catalyzed combustion section 14 through the method valve 19 of four from the hydrogen storage tank 16 with which it filled up with the hydrogen storing metal alloy. Thus, a catalyzed combustion reaction is performed within this catalyzed

combustion section 14 by air and hydrogen being supplied. Heat exchange of the combustion gas (exhaust gas) of the catalyzed combustion section 14 is carried out by heat exchangers E1 and E2, and it is discharged out of a system after that. If the temperature in the catalyzed combustion section 14 (380-800 degrees C) is stabilized, a bulb V3 will be opened, the water fed from feed-pump P will serve as a steam by the heat exchanger E2, and the steam-reforming section 13 will be supplied. And a compressor 11 is started while opening bulbs V1 and V2. Thereby, the hydrogen for hydrogenation desulfurization from the hydrogen storage tank 16 is added by the town gas supplied to the hydrogenation-desulfurization section 12 by the compressor 11. Then, heat exchange of town gas and the hydrogen for hydrogenation desulfurization is carried out by the heat exchanger E1, and they are carried out heating and a temperature up to 300-400 degrees C.

[0025] The reforming reaction in the steam-reforming section 13 and palladium membrane separation in the high grade hydrogen purification section 15 are started supplying town gas to the hydrogenation-desulfurization section 12 gradually. Each bulbs V4, V5, and V9 are opened after initiation of these reactions. Among these, by opening bulbs V4 and V9, the nontransparent gas of the palladium film passes a heat exchanger E4, the KO drum 17, heat exchangers E4 and E3, and the method valve 19 of four, and is supplied to the catalyzed combustion section 14. On the other hand, the high grade hydrogen which penetrated the palladium film is stored in the hydrogen storage tank 16 through a heat exchanger E3 by opening a bulb V5.

[0026] When a reaction within the hydrogenation-desulfurization section 12 and the steam-reforming section 13 is stabilized and high grade hydrogen comes to be stably refined within the high grade hydrogen purification section 15, bulbs V7, V8, and V12 are opened, and a bulb V6 is closed. Thus, high grade hydrogen is supplied to a fuel cell 18 from the hydrogen storage tank 16 through a bulb V7. On the other hand, the air besides a system is supplied to a fuel cell 18 through a bulb V12. Thereby, an ionic reaction occurs within a fuel cell 18, and electrical energy can be taken out to the exterior. Furthermore, the high grade hydrogen for a surplus is supplied to the catalyzed combustion section 14 through a bulb V8 through heat exchangers E4 and E3 and the method valve 19 of four from a fuel cell 18. And supply of the high grade hydrogen which goes to the catalyzed combustion section 14 from the hydrogen storage tank 16 is suspended by closing a bulb V6.

[0027] In addition, each reaction of the hydrogen manufacture in a system can be made to start easily by adopting a catalyzed combustion method in this way only by supplying the high grade hydrogen beforehand stored in the hydrogen storage tank 16 to the catalyzed combustion section 14 at the time of this system startup. Similarly, the hydrogen for hydrogenation desulfurization can also be supplied from the hydrogen storage tank 16. Thereby, the hydrogen bomb for desulfurization needed conventionally and the nitrogen gas cylinder at the time of starting become unnecessary. Consequently, effectiveness [, like a bomb exchange activity becomes unnecessary further], such as reduction of the installation area of a bomb and reduction of operation cost, is acquired. In addition, the bulb 14 in drawing is always closed at the time of this starting and operation.

[0028] Next, the actuation at the time of a halt is explained based on drawing 2 . As shown in drawing 2 , bulbs V5, V7, V8, and V12 are closed first, supply of the high grade hydrogen to the hydrogen storage tank 16 and supply of air are suspended, supply of the high grade hydrogen to a fuel cell 18 is suspended further, and the ionic reaction within a fuel cell 18 is stopped. Next, a bulb V11 is adjusted, the amount of supply of the air from the outside of a system is extracted gradually, and the oxygen density in the combustion gas from the catalyzed combustion section 14 is made into zero. Then, a bulb V14 is opened dropping the amount of supply of town gas on adjusting a bulb V1 gradually, and the combustion gas from the catalyzed combustion section 14 is gradually supplied into the system of reaction. At this time, the bulb V13 which is an exhaust air bulb of combustion gas is shut, and exhaust air of combustion gas is stopped. In addition, in order to prevent adjustment and a rapid temperature fall of the oxygen density of combustion gas, this catalyzed combustion section 14 may be supplied by using the town gas in the high grade hydrogen in the hydrogen storage tank 16, or a system as an auxiliary fuel by the bulb V6 and adjusting a bulb V10, if required. When it is inadequate in case adjustment of such an oxygen density reduces gradually the amount of the air supplied to the catalyzed combustion section 14 for example, it is for canceling a possibility that oxygen may be mixed accidentally and oxygen may be contained into systems, such as the steam-reforming section 13, in the combustion gas of the catalyzed combustion section 14.

[0029] And a bulb V1 is shut completely and supply of town gas is suspended. Furthermore, bulbs V2 and V3 are closed and supply of the hydrogen for hydrogenation desulfurization from the hydrogen storage tank 16 to into a system and supply of the steam into the system by feed-pump P are suspended. Subsequently, a

bulb V6 is closed (if required, a bulb V10 will also be closed), and supply in the catalyzed combustion section 14 of an auxiliary fuel is suspended. Then, the inflammable gas in a system is completely permuted by nitrogen, the carbon dioxide, and the steam, a bulb V11 is closed, and supply of the air to the catalyzed combustion section 14 is suspended. Furthermore, if the temperature in a system (steam-reforming section 13) falls to 100 degrees C or less, a compressor 11 will be suspended and all operations will be suspended. In addition, since the temperature at the time of a halt can remove the moisture in a system, lowering to ordinary temperature is desirable. In addition, when the gas in a system needs to be purged, a bulb V13 is opened wide, and if a barge is completed, all the bulbs V1-V14 will be closed. If all the bulbs V1-V14 are closed at this time, with the pressure in a system maintained, air will not flow in in a system from the exterior during a halt. Consequently, oxidation of a catalyst can be prevented at the time of next starting actuation.

[0030] As mentioned above, the combustion gas (exhaust gas) which does not contain oxygen is made to recycle into the system of reaction, lowering the concentration of inflammable gas gradually at the time of this system stop. Finally it is changed into nitrogen, a carbon dioxide, and a steam by this, and stops. Consequently, the bomb further for a permutation etc. is needlessness and ** in preventing especially the hydrogen embrittlement which membranous breakage produces in using metallic hydrogen demarcation membranes, such as palladium film, **** [, and]. [that activity falls] [preventing oxidization of a catalyst with the fault of generating a deadly poison at an elevated temperature in the case of the catalyst of a ruthenium system etc.] Moreover, by this catalyzed combustion method, since low concentration can also be oxidized, it is at the halt actuation time, and in case the concentration of inflammable gas is reduced gradually, incomplete combustion can be prevented and a combustion reaction can be continued.

[0031]

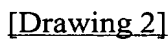
[Effect of the Invention] If it is in this invention, since starting and a halt of a hydrogen manufacturing installation can be performed without using a nitrogen gas cylinder and a hydrogen bomb, the effectiveness that the activity of reduction of operation cost or installation area, dangerous nitrogen, hydrogen bomb exchange, etc. becomes unnecessary can be acquired. Moreover, actuation of starting and a halt can also perform automation by constructing a sequence. Since the temperature up of the steam-reforming section is based on a catalyzed combustion method, they are miniaturization of equipment, and low NOx. Effectiveness, such as-izing, can also be acquired.

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[Drawing 1]



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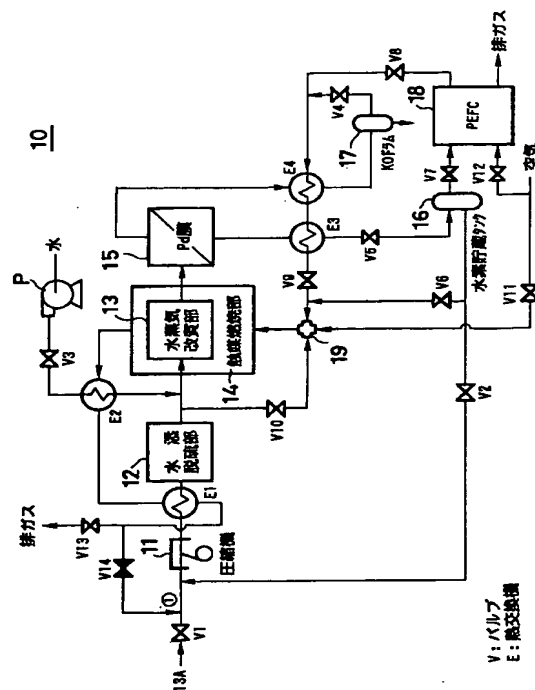
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(54)【発明の名称】 水素製造装置の起動方法およびその停止方法

(57)【要約】

【課題】 運転コストや設置面積の低減、危険な窒素および水素ボンベ交換などの作業が不要となるといった水素製造装置の起動方法およびその停止方法を提供する。

【解決手段】 起動時には、触媒燃焼部14に、水素貯蔵部16の高純度水素と空気とを供給して触媒燃焼反応を起こさせ、水蒸気改質部13を昇温させて水蒸気改質の開始温度に達したとき、水蒸気、水添脱硫用水素、原料炭化水素の供給を開始する。一方、停止時には、触媒燃焼部14中の酸素濃度を低下させ、燃焼ガスを反応系内にリサイクルさせて可燃性ガス濃度を徐々に低下させ、最終的に窒素、二酸化炭素、水蒸気に置換することで運転を停止する。その結果、運転コストや設置面積の低減、危険な窒素および水素ボンベ交換などの作業が不要となる。



【特許請求の範囲】

【請求項 1】 原料炭化水素の硫黄分を除去する脱硫部と、

上記脱硫部で脱硫された原料炭化水素に水蒸気を加えて水蒸気改質することで水素含有ガスを生成する水蒸気改質部と、

上記水素含有ガス中の水素を無機水素分離膜で透過して精製水素を製造する水素精製部と、

水素含有の可燃性ガスと空気中の酸素とを燃焼反応させて、上記水蒸気改質部を加熱する触媒燃焼部とを備えた水素製造装置の起動方法において、

上記触媒燃焼部に、上記水素精製部で精製された精製水素と空気とを供給して触媒燃焼反応を起こさせることで上記水蒸気改質部を昇温させ、

上記水蒸気改質部の温度が水蒸気改質の開始温度に達したとき、上記水蒸気および上記原料炭化水素の供給を開始する水素製造装置の起動方法。

【請求項 2】 上記精製水素は、燃料電池に供給される請求項 1 に記載の水素製造装置の起動方法。

【請求項 3】 上記脱硫部が、原料炭化水素に水添脱硫用水素を添加したのち、上記原料炭化水素中の硫黄分を脱硫して除去する水添脱硫部である請求項 1 または請求項 2 に記載の水素製造装置の起動方法。

【請求項 4】 上記水素精製部から得られた精製水素を貯蔵する水素貯蔵部を有する請求項 1～請求項 3 のうち、何れか 1 項に記載の水素製造装置の起動方法。

【請求項 5】 原料炭化水素の硫黄分を除去する脱硫部と、

上記脱硫部で脱硫された原料炭化水素に水蒸気を加えて水蒸気改質することで水素含有ガスを生成する水蒸気改質部と、

上記水素含有ガス中の水素を無機水素分離膜で透過して精製水素を精製する水素精製部と、

水素含有の可燃性ガスと空気中の酸素とを燃焼反応させて、上記水蒸気改質部を加熱する触媒燃焼部とを備えた水素製造装置の停止方法において、

上記触媒燃焼部への空気の供給量を徐々に下げて、該触媒燃焼部から排出された燃焼ガス中の酸素濃度を低下させ、

該触媒燃焼部からの燃焼ガスを水素製造装置の反応系内に供給し、

上記原料炭化水素と水蒸気の供給量を徐々に減らしながら、この反応系内の可燃性ガスの濃度を低下させ、

その後、上記触媒燃焼部への空気の供給を停止し、上記反応系内の温度が低下したのち上記水素製造装置を停止する水素製造装置の停止方法。

【請求項 6】 上記精製水素は、燃料電池に供給される請求項 5 に記載の水素製造装置の停止方法。

【請求項 7】 上記脱硫部が、原料炭化水素に水添脱硫用水素を添加したのち、上記原料炭化水素中の硫黄分を

脱硫して除去する水添脱硫部である請求項 5 または請求項 6 に記載の水素製造装置の停止方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水蒸気改質部を含む水素製造装置、または燃料電池システムやそれ以外の用途に用いられる水素製造装置の起動および停止方法に関する。

【0002】

【従来の技術】一般的な水素製造装置の起動・停止は、ポンペに充填された窒素などの不活性ガスを使用する。起動時は、ポンペより窒素を系内に流しながら、バーナなどで昇温、脱硫用の水添ガスとして水素ポンペより水素を供給する。停止時は、窒素で可燃性ガスを置換してから降温操作を行なう。この方式により、触媒の酸化や、パラジウム膜など金属膜の水素脆化を防止できるとともに、安全に操作を行なうことができる。しかしながら、この方式の欠点としては、窒素ポンペや水素ポンペなどが必要であり、コスト高、設置スペースが大きくなるという問題点がある。また、不活性ガスを切らしている場合には、起動・停止操作が行えず、ポンペの取り替えが面倒でかつ高圧であるため、危険である。そのほか、小型装置（例えば、家庭用や車載用燃料電池用水素製造装置）や諸事情などで、窒素ポンペや水素ポンペなどを設置できない場合も考えられ、さらに水素および窒素のインフラが整備されていないなどの問題点もある。

【0003】なお、原料炭化水素の供給を停止したのち、触媒が酸化しない程度まで徐々に降温してから、空気で置換する方法も考えられる。しかしながら、この方法によれば、可燃性ガス中に空気を供給するため、危険をともなうといった問題が懸念される。そのほか、水素を含有するガスがパラジウム膜などの無機水素分離膜へ低温で供給されるため、水素脆化が起こりやすい。その結果、無機水素分離膜の耐久性に乏しくなるという問題も懸念される。さらに、水蒸気改質部の加熱は、バーナの使用が一般的であるが、可燃性ガス濃度が低下すると燃焼が停止してしまうという問題点がある。

【0004】

【発明が解決しようとする課題】本発明は、このような従来技術を背景になされたもので、水素製造装置において、窒素ポンペや水素ポンペなどのポンペを必要としないので、コストの低減をはかることができ、またポンペの設置スペースが不必要となるため装置のコンパクト化が図れるとともに、面倒で危険をともなうポンペの取り替え作業に要する時間も削減できる水素製造装置の起動方法およびその停止方法を提供するものである。また、本発明は、ポンペを設置できない家庭用燃料電池や車載用燃料電池、およびその他の燃料電池、オンサイト水素製造装置などで、水素ポンペや窒素ポンペ、またバーナや、特別な電力などを使用せず、安全な水素製造装置の

起動方法およびその停止方法を提供することを、その目的としている。

【0005】

【課題を解決するための手段】請求項1に記載の発明は、原料炭化水素の硫黄分を除去する脱硫部と、上記脱硫部で脱硫された原料炭化水素に水蒸気を加えて水蒸気改質することで水素含有ガスを生成する水蒸気改質部と、上記水素含有ガス中水素を無機水素分離膜で透過して精製水素を製造する水素精製部と、水素含有の可燃性ガスと空気中の酸素とを燃焼反応させて、上記水蒸気改質部を加熱する触媒燃焼部とを備えた水素製造装置の起動方法において、上記触媒燃焼部に、上記水素精製部で精製された精製水素と空気とを供給して触媒燃焼反応を起こさせることで上記水蒸気改質部を昇温させ、上記水蒸気改質部の温度が水蒸気改質の開始温度に達したとき、上記水蒸気および上記原料炭化水素の供給を開始する水素製造装置の起動方法である。

【0006】請求項2に記載の発明は、上記精製水素は、燃料電池に供給される請求項1に記載の水素製造装置の起動方法である。

【0007】請求項3の発明は、上記脱硫部が、原料炭化水素に水添脱硫用水素を添加したのち、上記原料炭化水素中の硫黄分を脱硫して除去する水添脱硫部である請求項1または請求項2に記載の水素製造装置の起動方法である。

【0008】請求項4の発明は、上記水素精製部から得られた精製水素を貯蔵する水素貯蔵部を有する請求項1～請求項3のうち、何れか1項に記載の水素製造装置の起動方法である。

【0009】請求項5に記載の発明は、原料炭化水素の硫黄分を除去する脱硫部と、上記脱硫部で脱硫された原料炭化水素に水蒸気を加えて水蒸気改質することで水素含有ガスを生成する水蒸気改質部と、上記水素含有ガス中の水素を無機水素分離膜で透過して精製水素を精製する水素精製部と、水素含有の可燃性ガスと空気中の酸素とを燃焼反応させて、上記水蒸気改質部を加熱する触媒燃焼部とを備えた水素製造装置の停止方法において、上記触媒燃焼部への空気の供給量を徐々に下げて、該触媒燃焼部から排出された燃焼ガス中の酸素濃度を低下させ、該触媒燃焼部からの燃焼ガスを水素製造装置の反応系内に供給し、上記原料炭化水素と水蒸気の供給量を徐々に減らしながら、この反応系内の可燃性ガスの濃度を低下させ、その後、上記触媒燃焼部への空気の供給を停止し、上記反応系内の温度が低下したのち上記水素製造装置を停止する水素製造装置の停止方法である。

【0010】請求項6に記載の発明は、上記精製水素は、燃料電池に供給される請求項5に記載の水素製造装置の停止方法である。

【0011】請求項7の発明は、上記脱硫部が、原料炭化水素に水添脱硫用水素を添加したのち、上記原料炭化

水素中の硫黄分を脱硫して除去する水添脱硫部である請求項5または請求項6記載の水素製造装置の停止方法である。

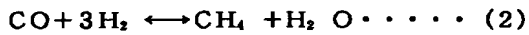
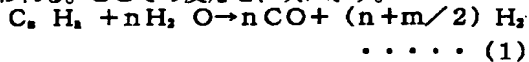
【0012】

【発明の実施の形態】発明の実施の形態を図面に基づいて説明する。図1は、本発明の一実施の形態に係る水素製造装置の起動方法を示す系統図である。図2は、本発明の一実施の形態に係る水素製造装置の停止方法を示す系統図である。図1において、符号10は、都市ガス、LPG、灯油、メタノールなどを原料とする水素製造装置である。なお、ここでは、都市ガスを採用している。以下、この水素製造装置10の各構成部を説明する。符号11は、都市ガスを水添脱硫部（脱硫部）12へ供給する圧縮機である。この水添脱硫部12は、上流側の水素化触媒層と、下流側の脱硫剤層とに分かれている。水添脱硫部12では、圧縮機11により供給された都市ガスに、後述する高純度水素精製部（水素精製部）15のパラジウム膜（無機水素分離膜）を透過して得られた高純度水素（精製水素）の一部を水添脱硫用水素として添加することにより、都市ガス中の硫黄分が脱硫される。

【0013】水素化触媒としては、ニッケルモリブデンまたはコバルトモリブデンなどの酸化物、または硫化物をシリカやアルミナなどの担体に担持させたNiMo触媒またはCoMo触媒などが挙げられる。低圧下では、ニッケルモリブデン触媒が好ましい。また、脱硫剤としては、酸化亜鉛やニッケル系収着剤などが単独または適宜担体に担持して用いられる。水素化触媒層では、原料炭化水素中の硫黄分が水素化されて硫化水素が生成する。その反応温度は、300～400℃であり、高純度水素を用いて脱硫を行なうことで、脱硫効果も上がり、改質触媒の寿命も延びることになる。脱硫剤層では、例えば、 $\text{H}_2\text{S} + \text{ZnO} = \text{ZnS} + \text{H}_2\text{O}$ の反応が起きる。なお、脱硫後の原料炭化水素は、水蒸気改質部13に供給される。ここでは、原料炭化水素中の硫黄化合物を水添脱硫方法を採用したが、そのほか例えば硫黄化合物を、直接、触媒に吸着させる方法でもよい。この場合の触媒としては、例えばニッケル、亜鉛、銅などの金属やその酸化物、または硫化物、さらにはゼオライトや活性炭などが挙げられる。活性炭としては、ナトリウムなどのアルカリ金属を添着したもの、臭素を吸着した活性炭などを使用することができる。

【0014】この水蒸気改質部13は、脱硫された都市ガスに水または水蒸気を添加し、さらに改質触媒を接触させて水蒸気改質することで、高濃度水素含有ガスを製造する。この水蒸気改質部13には、ルテニウムまたはニッケルなどの元素をアルミナ、シリカなどの担体に担持した改質触媒が充填されている。このうち、ルテニウム系触媒の方が、炭素数の多い灯油などの原料を使用する場合は、炭素析出を抑制できるので好ましい。水蒸気改質部13では、脱硫された炭化水素の水蒸気改質が行

なわれる。ここでの反応を、次に示す。



【0015】符号14は、水蒸気改質部13の周囲に外装されて、水素と空気中の酸素とを触媒燃焼させる触媒燃焼部である。なお、触媒燃焼部14は、水蒸気改質部13に内装されていてもよく、さらには、伝熱性の高い熱交換型の反応器などでもよい。触媒燃焼部14の触媒としては、アルミナなどに白金、パラジウムなどを担持した触媒が用いられる。水素製造装置10の起動時の水蒸気改質部13の温度は、380℃以上、例えば380～500℃である。380℃未満では反応転化率が低く、また水素、メタン、一酸化炭素などを含む可燃性ガスを触媒燃焼部で再利用する際に、これらの可燃性ガスの酸化反応が進まないという不都合が生じる。そして、最終的には800℃位が好ましい。

【0016】好ましい水蒸気の添加割合は、水蒸気/原料(S/C)2.4～3.0kg-mol-H₂O/kg-mol-Cである。さらに好ましくは、2.5～2.8kg-mol-H₂O/kg-mol-Cである。2.4kg-mol-H₂O/kg-mol-C未満では、都市ガスの反応転化率が低くなり、水素精製量が低下するとともに炭素も析出しやすくなる。一方、3.0kg-mol-H₂O/kg-mol-Cを超えると、都市ガスの反応転化率は高まるが、スチーム量が多くて水素分圧が低下するのでパラジウム膜による水素膜分離には不利である。

【0017】符号15は、高濃度水素含有ガス中の水素をパラジウム膜で透過して高純度水素を精製する高純度水素精製部である。無機水素分離膜としては、このパラジウム膜のほかに、パラジウムと銀、銅、ニッケル、イットリウムなどとの合金からなるパラジウム合金膜などを、単独またはセラミックス製、ガラス製、ステンレスなどの各種の多孔質担体に被覆したものや、ゼオライト膜などが採用できる。

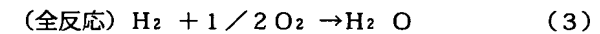
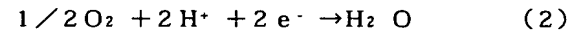
【0018】符号16は、高純度水素精製部15から得られた高純度水素を貯蔵する水素貯蔵タンク(水素貯蔵部)である。水素貯蔵タンク16は、起動時に触媒燃焼用および水添ガス用に必要な量の水素を貯蔵できるものとし、コンパクト化を図るため、水素吸蔵合金が充填されたタンクが好ましい。

【0019】符号17は、上記パラジウム膜の非透過ガスを冷却して、このガス中に含まれる水分を除去するKO(ノックアウト)ドラムである。

【0020】符号18は、水素貯蔵タンク16に一時貯蔵された高純度水素が供給される固体高分子型燃料電池(以下、燃料電池18という)である。その用途としては、例えば家庭用燃料電池、車載用燃料電池などが挙げ

られる。この燃料電池18は、電解質材料を有している。この電解質材料は、一般にイオン交換基としてスルホン酸基をもつ高分子イオン交換膜を有する。セルに水素(燃料)、酸素(酸化剤)を供給すると、次式の反応によって電気エネルギーを外部へ取り出すことができる。

【0021】



式(1)によって生成された水素イオンは、高分子イオン交換膜中のイオン交換基を介して水(xH₂O)とともに移動し、式(2)のように酸素と反応して水(H₂O)を生成する。不純物が除去された高純度水素は、水分調整されたのちに燃料電池18に供給され、ここで水を生成しながら電気エネルギーが得られる。燃料電池18のセルには高純度水素が供給されるので、一酸化炭素による電極被毒はなく、性能低下は防止できる。また、セルの排ガスは、触媒燃焼部14に供給させ、反応系内の熱源として利用される。そのほか、水添脱硫用水素としても再利用することができる。なお、この燃料電池18から排出された空気(酸素)を触媒燃焼部14に供給してもよい。

【0022】記号E1は、圧縮機11から水添脱硫部12に供給される都市ガスと、触媒燃焼部14からの燃焼ガスとを熱交換して、都市ガスを300～400℃の水添脱硫温度まで高める熱交換器である。記号E2は、水蒸気改質部13に供給ポンプPにより供給される水と、触媒燃焼部14からの燃焼ガスとを熱交換して、水蒸気改質用の水蒸気を発生させる熱交換器である。記号E3は、燃料電池18から触媒燃焼部14に供給される高純度水素の余剰分およびパラジウム膜の非透過ガスと、パラジウム膜を透過した高温の高純度水素とを熱交換する熱交換器である。記号E4は、燃料電池18から触媒燃焼部14に供給される高純度水素の余剰分およびパラジウム膜の非透過ガスと、パラジウム膜の高温の非透過ガスとを熱交換する熱交換器である。熱交換器E3とE4により触媒燃焼部14に再利用される水素、メタン、一酸化炭素を含む可燃性ガスは、380℃以上に加熱・昇温される。380℃未満では、メタンなどの可燃性ガスの酸化反応が円滑に行われないからである。

【0023】なお、ここでの水素製造装置10は、圧縮機11、水添脱硫部12、水蒸気改質部13、触媒燃焼部14、高純度水素精製部15、水素貯蔵タンク16より構成されている。しかしながら、水蒸気改質部13の後段に図示しないガス変成部を設けてもよい。また、水蒸気改質部13と高純度水素精製部15を一体化したメンブレンリアクタにしてもよく、さらには、水蒸気改質部13の後段に、CO変成部と高純度水素精製部15を一体化したメンブレンリアクタを設けてもよい。図中、

符号19は、4方弁形式の流路切り換え装置（以下、4方弁という）である。

【0024】上記構成の水素製造装置10の起動方法およびその停止方法について、以下詳述する。まず、図1に基づき、起動時の操作を説明する。図1に示すように、バルブV11を開き、系外の空気を4方弁19を経て触媒燃焼部14に供給する。次いで、バルブV6を開いて、水素吸蔵合金が充填された水素貯蔵タンク16から高純度水素を、4方弁19を介して触媒燃焼部14に供給する。このようにして、空気と水素が供給されることで、この触媒燃焼部14内で触媒燃焼反応が行われる。触媒燃焼部14の燃焼ガス（排ガス）は、熱交換器E1、E2により熱交換され、その後、系外へ排出される。触媒燃焼部14内の温度（380～800℃）が安定したなら、バルブV3を開いて、供給ポンプPから圧送された水が熱交換器E2によって水蒸気となり、水蒸気改質部13に供給される。それから、バルブV1、V2を開くとともに圧縮機11を起動する。これにより、水素貯蔵タンク16からの水添脱硫用水素が、圧縮機11によって水添脱硫部12に供給される都市ガスに添加される。その後、都市ガスおよび水添脱硫用水素は、熱交換器E1によって熱交換され、300～400℃まで加熱・昇温される。

【0025】都市ガスを水添脱硫部12に徐々に供給しながら、水蒸気改質部13における改質反応と、高純度水素精製部15におけるパラジウム膜分離とを開始する。これらの反応の開始後、各バルブV4、V5、V9を開く。このうち、バルブV4、V9を開弁することで、パラジウム膜の非透過ガスが、熱交換器E4、KODラム17、熱交換器E4、E3および4方弁19を通過して触媒燃焼部14に供給される。一方、バルブV5を開弁することで、パラジウム膜を透過した高純度水素が熱交換器E3を経て水素貯蔵タンク16に貯蔵される。

【0026】水添脱硫部12内および水蒸気改質部13内での反応が安定し、高純度水素精製部15内で高純度水素が安定的に精製されるようになったとき、バルブV7、V8、V12を開き、バルブV6を閉じる。このようにして、バルブV7を介して水素貯蔵タンク16から燃料電池18に高純度水素が供給される。一方、バルブV12を介して、系外の空気が燃料電池18に供給される。これにより、燃料電池18内でイオン反応が発生して、外部へ電気エネルギーを取り出すことができる。さらに、バルブV8を介して、燃料電池18から余剰分の高純度水素が、熱交換器E4、E3、4方弁19を通過して触媒燃焼部14へ供給される。そして、バルブV6を閉弁することで、水素貯蔵タンク16から触媒燃焼部14へ向かう高純度水素の供給が停止される。

【0027】なお、このシステム起動時には、このように触媒燃焼方式を採用することで、あらかじめ水素貯蔵

タンク16に貯蔵された高純度水素を触媒燃焼部14に供給するだけで、容易に系内の水素製造の各反応を開始させることができる。同様に、水添脱硫用水素も水素貯蔵タンク16より供給することができる。これにより、従来必要とされていた脱硫用の水素ポンプおよび起動時の窒素ポンプが不要となる。その結果、ポンプの設置面積の低減や運転コストの低減など、さらにはポンプ交換作業が不要になるなどの効果が得られる。なお、図中のバルブ14は、この起動時および運転時において常時閉じている。

【0028】次に、図2に基づいて、停止時の操作を説明する。図2に示すように、まずバルブV5、V7、V8、V12を閉じ、水素貯蔵タンク16へ的高純度水素の供給と空気の供給とを停止し、さらに燃料電池18へ的高純度水素の供給を停止して、燃料電池18内でのイオン反応を停止させる。次に、バルブV11を調整して、系外からの空気の供給量を徐々に絞り、触媒燃焼部14からの燃焼ガス中の酸素濃度をゼロにする。続いて、バルブV1を調整することで、都市ガスの供給量を徐々に落としながらバルブV14を開き、触媒燃焼部14からの燃焼ガスを反応系内へ徐々に供給する。このとき、燃焼ガスの排気バルブであるバルブV13を閉めて燃焼ガスの排気を停止する。なお、燃焼ガスの酸素濃度の調整や急激な温度低下を防止するため、バルブV6および必要ならばバルブV10を調整することで、水素貯蔵タンク16内の高純度水素や系内の都市ガスを補助燃料としてこの触媒燃焼部14へ供給してもよい。このような酸素濃度の調整は、触媒燃焼部14に供給される空気の量を徐々に減らしていく際、例えばそれが不十分な場合には、触媒燃焼部14の燃焼ガス中に誤って酸素が混入されてしまい、水蒸気改質部13などの系内へ酸素が含まれる恐れを解消するためである。

【0029】そして、バルブV1を完全に閉めて都市ガスの供給を停止する。さらに、バルブV2、V3を開弁して、水素貯蔵タンク16から系内への水添脱硫用水素の供給、および、供給ポンプPによる系内への水蒸気の供給を停止する。次いで、バルブV6を閉じ（必要であれば、バルブV10も閉じる）、補助燃料の触媒燃焼部14への供給を停止する。続いて、系内の可燃性ガスを、完全に窒素、二酸化炭素および水蒸気に置換し、バルブV11を閉弁して触媒燃焼部14への空気の供給を停止する。さらに、系内（水蒸気改質部13）の温度が100℃以下まで低下したなら、圧縮機11を停止し、全ての運転を停止する。なお、停止時の温度は、系内の水分が除去できるので、常温まで下げるのが好ましい。なお、系内のガスをバージする必要がある場合には、バルブV13を開放し、バージが終了したなら全てのバルブV1～V14を開弁する。このとき、系内の圧力を保ったまま全てのバルブV1～V14を閉弁すれば、停止中に外部から空気が系内に流れ込むことがない。その結

果、次回の起動操作時に触媒の酸化を防止することができる。

【0030】以上のように、このシステム停止時には、徐々に可燃性ガスの濃度を下げながら、酸素を含まない燃焼ガス（排ガス）を反応系内へリサイクルさせる。これにより、最終的に窒素と二酸化炭素と水蒸気に変換され停止する。その結果、活性が低下したり、特にルテニウム系の触媒などの場合には高温で猛毒を発生するなどの不具合がある触媒の酸化を防止したり、またパラジウム膜などの金属水素分離膜を使用する場合には膜の破損が生じる水素脆化を防止したり、さらに置換用のポンペなどが不要となる。また、この触媒燃焼方式では低濃度でも酸化反応を行えるため、停止操作時で可燃性ガスの濃度を徐々に減らしていく際に、不完全燃焼を防止し、燃焼反応を継続することができる。

【0031】

【発明の効果】本発明にあっては、窒素ポンペ、水素ポンペを使用せずに水素製造装置の起動・停止が行えるので、運転コストや設置面積の低減、危険な窒素および水

素ポンペ交換などの作業が不要となるといった効果を得ることができる。また、起動・停止の操作は、シーケンスを組むことで自動化も行なうことができる。水蒸気改質部の昇温が触媒燃焼方式によるため、装置のコンパクト化、低NO_x化などの効果も得ることができる。

【図面の簡単な説明】

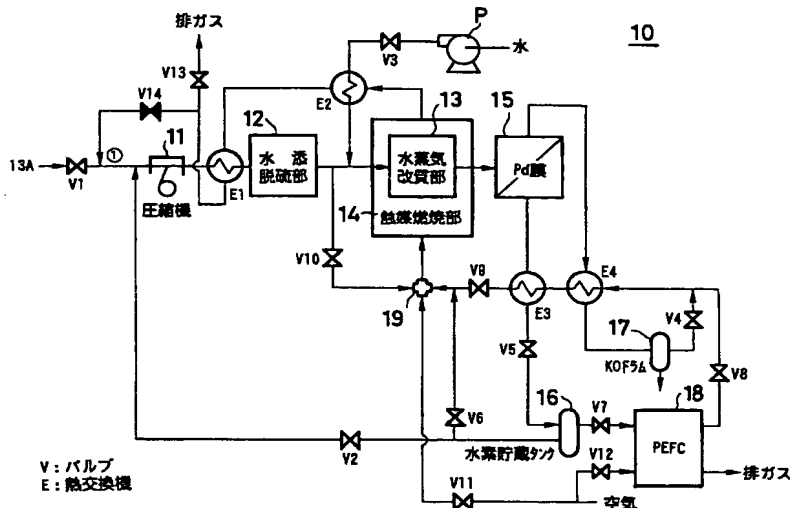
【図1】本発明の一実施の形態に係る水素製造装置の起動方法を示す系統図である。

【図2】本発明の一実施の形態に係る水素製造装置の停止方法を示す系統図である。

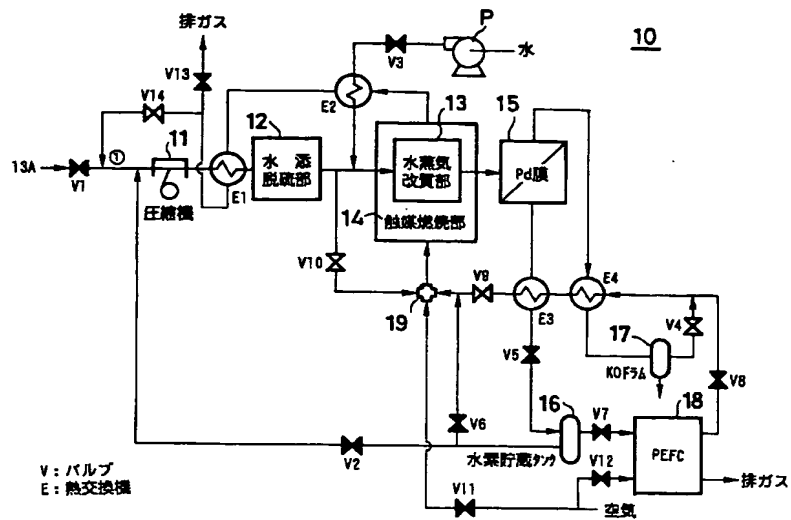
【符号の説明】

- 10 水素製造装置
- 11 圧縮機
- 12 水添脱硫部（脱硫部）
- 13 水蒸気改質部
- 14 触媒燃焼部
- 15 高純度水素精製部（水素精製部）
- 16 水素貯蔵タンク（水素貯蔵部）
- 18 固体高分子型燃料電池（燃料電池）

【図1】



【図2】



フロントページの続き

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